

# COATINGS AND ENAMELS

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## USE OF ADDITIONS OF FERROELECTRIC SUBSTANCES TO IMPROVE THE DIELECTRIC PROPERTIES OF GLASS ENAMELS

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It is shown that there is promise in introducing ferroelectric additives to glass enamel coatings to improve their dielectric characteristics. The limits of the additive introduced for low-alkali borosilicate enamel are determined. A comparative table of properties of the initial and composite enamels is presented. The dielectric properties of the new material are determined and it is determined that the additive does not dissolve in the glass enamel.

**Key words:** glass enamel, dielectric barrier, additions of ferroelectric substances, increase of permittivity.

Modern society had long been concerned with ecological conditions and finding new ways for solving these problems. For this reason work on preserving and maintaining the ecology of our planet for future generations and on knowledgeable use of resources and setting new ecological standards will always be topical. The present situation is increasingly attracting the attention of researchers and specialists in different areas of science.

A qualitatively new direction in the sphere of cleaning and neutralizing different media is the use of chemical reagents, such as ozone. The role of ozone today is so great that the International Antidioxine Association has proposed an evaluation of the degree of industrial development and advancement of governments with respect to the amount of ozone produced or used by them [1].

The main advantages of ozone over other reagents (for example, compounds of chlorine and hydrogen peroxide) are: high oxidative power; elevated activity with respect to bacteria, viruses, and many other pathogenic microorganisms; ecological cleanliness; better as compared with other reagents indicators for odor, taste, and color of water after treatment.

Owing to its exceptional properties ozone is widely used in the most diverse areas of the national economy, but this pertains primarily to Western Europe and the USA. In Russia

ozonization technology is being introduced in centralized water treatment systems and in industrial objects (Moscow, Nizhny Novgorod, Perm, the Republic of Tatarstan, and others).

The application of ozone is limited to its use in water purification systems. The main areas of application of ozone are: water conditioning systems; petrochemical, microbiological, cellulose-paper, food and light industry; nonferrous metallurgy; agriculture; machine building; and, atomic energy.

Mass adoption of ozonization technology is impeded by the quite high cost of energy required to obtain ozone (on average, 10–16 kW · h/kg O<sub>3</sub>). For this reason a great deal of attention is being devoted to develop and improve the construction of ozone generators and the materials use to fabricate their main working elements.

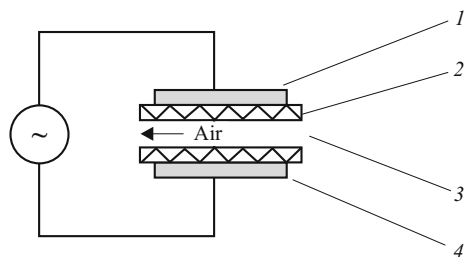
The most economically cost-effective and applicable on commercial scales is the technology of obtaining ozone based on using a special electric discharge — a dielectric barrier discharge (DBD).

Ozone is synthesized under the action of an ac voltage in a medium of pure oxygen or oxygen-air mixture passing through a discharge gap formed by two electrodes, at least one of which is covered with a dielectric. This arrangement is shown schematically in Fig. 1.

Many factors influence the productivity of an ozonizer. Examples are the characteristics of the dielectric, owing to which the required form of the discharge (barrier discharge) is obtained.

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**Fig. 1.** Arrangement of an ozone generator: 1) high-voltage electrode; 2) dielectric barrier; 3) discharge gap; 4) grounded electrode.

The materials used as a dielectric barrier are glasses and in special cases ceramic materials and thin layers of enamel or polymers.

Compared with all other materials, glass enamels, aside from having satisfactory dielectric and thermomechanical characteristics, are less expensive because a thin layer of a glass coating is used. This gives advantages over ozonizers with a difference type of dielectric barrier. In addition, for ozonizers with enameled electrodes, bilateral cooling of the electrodes can be used, thereby ensuring more intense heat removal from the discharge gap, eliminating the decomposition of ozone due to overheating, and decreasing the discharge gap, which will increase the working voltage in the electrode system.

Ozonizer manufacturers have now formulated a number of requirements which a dielectric must meet in order to generate a DBD: elevated values of the permittivity — 10 – 25; dielectric losses no more than 0.01; high electric resistance — of the order of  $10^{-10} \Omega \cdot \text{cm}$ . In addition, good thermal conductivity of the material is also required to ensure rapid cooling of the working flux. For glass enamel coatings, one of the main requirements is strong bonding of the coating and electrode material. Stainless steel (12Kh18N10T) with  $\text{CLTE} = 170 \times 10^{-7} \text{ K}^{-1}$  is often used as an electrode material. For this reason, to match the coating and metal the CLTE of the glass enamel must not be lower than  $120 \times 10^{-7} \text{ K}^{-1}$ .

The requirements for the dielectric properties are not accidental. They follow from the study of the kinetics of the synthesis of ozone in a DBD. The active power of a barrier discharge and therefore the specific energy factor in a barrier discharge are directly proportional to the product of the frequency of the supply voltage by the capacitance of the dielectric barriers. Hence, the active power of a barrier discharge can be increased not only by increasing the frequency of the supply voltage but also by using a dielectric with a high specific capacitance [2]. Hence factors affecting the efficiency of ozonizers are the dielectric properties of the barrier.

One method for increasing the operating efficiency could be the choice of material for the dielectric barrier, which determines the form of the discharge for which the ozone yield is highest. For this it is necessary to establish a clear connection

between the properties of ozonizers, the structure of the discharge, and ozone yield.

It can be quite difficult to attain a combination in glassy material of high CLTE and  $\epsilon$  of low dielectric losses and electric conductivity by varying the chemical composition. In this case, additives which will impart the necessary properties to the glass matrix can be added to the matrix. In this way a material that meets the necessary requirements can be obtained.

Many works where ferroelectrics are added to a glass matrix are encountered in the scientific literature [3, 4, 5, 6]. The use of such materials is not always related with the process of obtaining ozone. Niobates and titanates of various metals are used as fillers. The amount of filler introduced was varied from 25 to 40%.<sup>3</sup> The introduction of these additives made it possible to improve the dielectric characteristics of the materials, for example, increase the permittivity by a factor of 2 – 2.5.

For this reason the use of ferroelectric materials as fillers in glass enamels used as dielectric barriers in ozone generators merits close attention.

About 800 different ferroelectric compounds, mainly oxides, are now known. Before proceeding directly to the selection of ferroelectric materials which can be used as fillers in electrically insulating enamels, the requirements which they must meet should be listed.

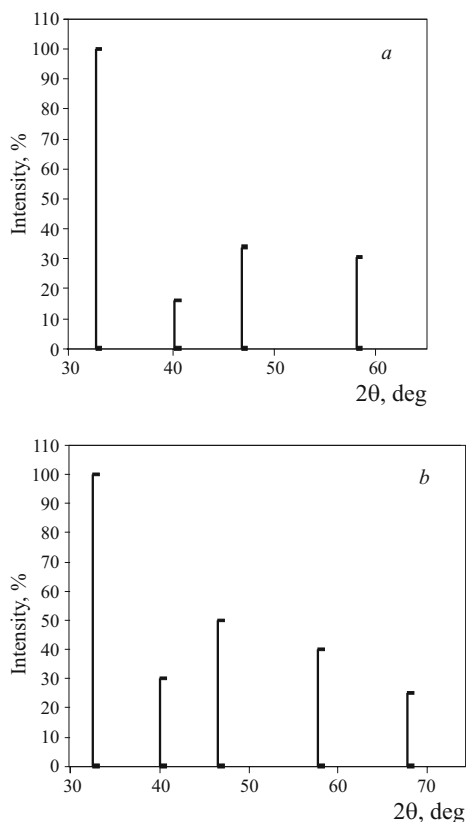
The choice of a material which can be used as an additive introduced into the initial glass enamel must be based on the following requirements:

- the CLTE of the filler must match that of the initial glass matrix to prevent stresses which can arise during the formation of the coating;
- the material introduced into the initial enamel should not undergo any phase transitions, polymorphic transformations or other structural changes in the formation interval and the working temperature range of the composite coating; it is reported in [5] that ferroelectrics which undergo a phase transition into a spontaneously polarized state below or near 293 K should be used as fillers in such coatings; in this case the permittivity of the composite material remains constant the working temperature range of the electrodes (20 – 100°C), while the dielectric losses are low; in addition, such ferroelectrics retain high values of  $\alpha$  at high frequencies, which is also important;
- the filler must not interact with the glass matrix during the formation of the coating.

Previous research on coatings, to which ferroelectric substances are added, points to several compounds: barium metatitanate, strontium metatitanate, sodium niobate, and lead titanate.

In the present work strontium titanate is used as the additive. The choice of this particular ferroelectric as a filler is not accidental. This compound does not exhibit phase transformation in the interval of coating deposition onto stainless

<sup>3</sup> Here and below — content by weight.



**Fig. 2.** X-ray diffraction pattern of synthesized strontium metatitanate (a) and strontium metatitanate according to the ASTM 1999 card file (b).

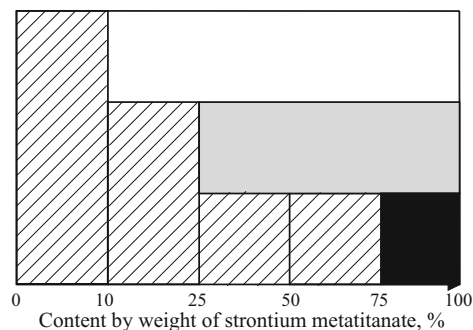
steel. Strontium titanate is a paraelectric at room temperature, retaining high permittivity and low dielectric losses:  $\epsilon = 250$  and  $\tan \delta = 0.00025$  above the Curie point. A structural phase transition is observed at  $105^\circ\text{C}$ . In addition, the CLTE of strontium titanate is close to that of enamels used for stainless steel — it equals  $94 \cdot 10^{-7} \text{ K}^{-1}$  [7].

The objective of the present work is to develop a material on the basis of a glassy matrix and filler in the form of strontium metatitanate which can combine high indicators of dielectric and technological properties.

Glass compositions based on low-alkali ( $R_2O < 5\%$ ) borosilicate glass with elevated content of alkali-earth metal oxides (RO about 60%) as well as additives which improve the melting properties of glass enamels ( $\text{Na}_3\text{AlF}_6$ ,  $\text{CaF}_2$ ,  $\text{MnO}$ ,  $\text{MO}_3$ ) and bonding oxides ( $\text{NiO}$ ,  $\text{Co}_2\text{O}_3$ ) were used as matrices (here and below shall refer to the initial glass in this manner).

#### Properties of the Initial Glass Enamel

CLTE, $10^{-7} \text{ K}^{-1}$ . . . . .	130
Permittivity $\epsilon$ . . . . .	8
Tangent of the dielectric loss angle $\tan \delta$ (at 1 kHz) . . . . .	0.003
Softening temperature $T_g$ , $^\circ\text{C}$ . . . . .	670
Deposition temperature, $^\circ\text{C}$ . . . . .	840



**Fig. 3.** Degree of melting of the composite coatings as a function of the content of strontium metatitanate: □) complete melting; ▨) incomplete melting; ■) no melting.

Strontium metatitanate was obtained by sintering the initial substances: strontium carbonate and titanium dioxide at  $1300^\circ\text{C}$  with soaking for 4 h at the maximum temperature. The components were taken in the proportion 1 : 1. Figure 2 shows that the x-ray diffraction pattern obtained for strontium titanate  $\text{SrTiO}_3$  and for comparison the same for strontium metatitanate according to the ASTM 1999 card deck. One can see that the material obtained is strontium titanate but with an admixture of rutile.

The filler was introduced into the frit of the glass matrix in the amounts 10, 25, 50, and 75%. The mixture obtained was carefully mixed. The average particle size was  $7 \mu\text{m}$  for the glass enamel powder 10 and  $7 \mu\text{m}$  for  $\text{SrTiO}_3$ .

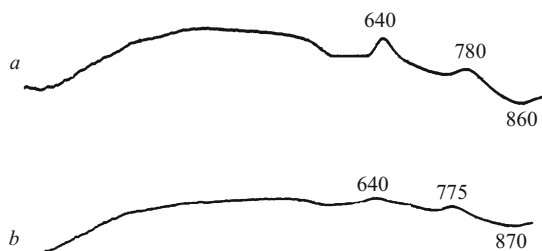
The dry method of enameling was chosen for deposition. In this method, the surface of a steel plate is covered by glass enamel powder in form of a thin layer by powdering an initially heated surface of the substrate.

Stainless steel (12Kh18N10T) was used as the substrate. Before the coating as applied the surfaces of the steel plates were worked as follows: mechanical working → heat-treatment ( $760^\circ\text{C}$ , 15 min) → mechanical working → washing (distilled water) → chemical decontamination (organic solvent) → washing (distilled water) → chemical decontamination (ethyl alcohol).

To determine the optical enameling regime the coatings were fired at different temperatures and with different soaking times. It was established that to obtain composite coatings based on the glass matrix used the optimal deposition conditions are as follows: deposition temperature  $860^\circ\text{C}$ , soaking time 3 min, and number of layers 3.

The results are presented in Fig. 3. The degree of melting was estimated conditionally according to the form of the coatings.

Finally, coatings with the required quality were obtained with strontium metatitanate content 10 and 25%; in all other cases this could not be achieved. The thermal shock method was used to determine the strength of the bonding of the steel substrate with the enamel coating deposited on it. The experiment showed that the strength of the bond between the



**Fig. 4.** Differential-thermal analysis: *a*) initial glass enamel; *b*) glass enamel with 19% metatitanate.

enamel and the material is high and the heat resistance of the is no lower than 280°C, since the coatings remained in their initial form after a thermal shock right up to 280°C.

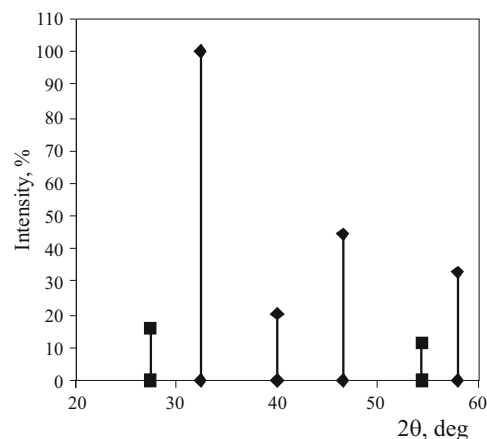
Thus, further studies are best done only for glass enamels with SrTiO<sub>3</sub> content of 10 and 25%. For them, measurements of the dielectric properties were performed for them; the results are presented in Table 1.

We note that the values of the permittivity increased by a factor of approximately 2 – 2.5 with the values of  $\tan \delta$  remaining acceptable as compared with the initial glass.

DTA analysis was performed to determine whether or not the additive dissolved in the glass enamel (the results are presented in Fig. 4). The DTA curves of the experimental material exhibits two exothermic peaks and one endothermic peak; these same peaks are observed in glass enamel with added strontium titanate, only with lower intensity, which indicates the inertness of the additive as compared with the glass matrix. This result is confirmed by the lines corresponding to strontium titanate and some portion of titanium dioxide in the x-ray line pattern of glass enamels with additives (Fig. 5).

It can be supposed on this basis that this material is a glass in which strontium metatitanate particles are distributed. Thus the properties of the material will consist of the properties of the material and filler. Correspondingly, in an electric field the glass matrix and strontium metatitanate contribute to the values of the dielectric properties.

It is known that in glassy materials electric conduction is due to predominately the ions of alkali metals because of the small radius and their position as modifiers. As concerns the glass enamels studied in the present work, it can be assumed that here charge transfer is also due to the ions of alkali elements. The ions of alkali-earth metals, which total content in



**Fig. 5.** X-ray phase analysis of glass enamels with added strontium metatitanate: ■) SrTiO<sub>3</sub> crystal phase; ◆) TiO<sub>2</sub> crystal phase.

this glass reaches 60%, can be responsible to a lesser degree for the electric conductivity of the glass enamels with the present composition, since they are represented by a large ionic radius (Ba, Ca, Cd, and others). The values of the  $\tan \delta$  of the angle of dielectric losses mainly depend on the electric conductivity of the glass. Therefore, in the experimental materials it is precisely the glass matrix and not crystalline strontium titanate that is responsible for the transfer of electric charge. In a crystal, ions must overcome a higher potential barrier in order to occupy a new position in the lattice than ions of the glassy matrix. On the basis of these assumptions it would be worthwhile to expect  $\tan \delta$  to decrease or changes in the values of the dielectric losses to be absent ( $\tan \delta$  of strontium titanate is  $2.5 \times 10^{-4}$ ). But experiment shows the reverse —  $\tan \delta$  increases from 0.003 to 0.005. Apparently, this can be explained by the fact that because of the difference of the thermal expansion coefficients of the materials microcracks and cracks can form on the boundaries between large grains of additive and the glass-enamel matrix as the material cools. The presence of such defects made a definite contribution to the value of  $\tan \delta$ .

An increase of the permittivity of the coating obtained from 8 to 18 (taking account samples with  $\tan \delta$  corresponding to the requirements) is also observed. This increase can be attributed only to SrTiO<sub>3</sub>. Strontium metatitanate is present in glass in a nonpolar paraelectric phase, whose permittivity is of the order of 250. This means that when an electric field is applied SrTiO<sub>3</sub> crystals make the largest contribution to the polarization.

As a result it can be said that the introduction of ferroelectric materials into a glass matrix made it possible to attain the goal, specifically, the permittivity as compared with the initial glass increased by a factor of 2 – 2.5. Low values of the dielectric losses can be retained by introducing SrTiO<sub>3</sub> in amount to greater than 10%. Hence it follows that further work is best done only with a small amount of the additive. It is also worthwhile to pay close attention to the technology

**TABLE 1.** Dielectric Characteristics of Composite Coatings

Indicator	Initial glass enamel	Composite coating with SrTiO <sub>3</sub> content, wt. %	
		10	25
Dielectric losses			
$\tan \delta$ (at 1 kHz)	0.003	0.005	0.019
Permittivity $\epsilon$	8	18	26

used to obtain the material so as to prevent the formation of defects and pores, which can contribute to the dielectric losses.

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